NASA TECHNICAL NOTE

NASA TN D-3503

NASA TN D-3503

INFLUENCE OF TIME ON VACUUM VAPORIZATION RATE AND SURFACE COMPOSITIONAL STABILITY OF TANTALUM CARBIDE - HAFNIUM CARBIDE SOLID SOLUTIONS ABOVE 2000° C

by Daniel Deadmore

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JULY 1966

INFLUENCE OF TIME ON VACUUM VAPORIZATION RATE AND SURFACE COMPOSITIONAL STABILITY OF TANTALUM CARBIDE - HAFNIUM CARBIDE SOLID SOLUTIONS ABOVE 2000° C

By Daniel Deadmore

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – Price $1.00

INFLUENCE OF TIME ON VACUUM VAPORIZATION RATE AND SURFACE COMPOSITIONAL STABILITY OF TANTALUM CARBIDE - HAFNIUM CARBIDE SOLID SOLUTIONS ABOVE 2000° C

by Daniel Deadmore

Lewis Research Center

SUMMARY

The vaporization rates of tantalum carbide (TaC), hafnium carbide (HfC), and of solid solutions of 80TaC·20HfC, 50TaC·50HfC, and 25TaC·75HfC were determined gravimetrically as functions of heating times from 5 to 70 hours in vacuum at several temperatures between 2060° and 2600° C. After the samples were heated, they were examined by X-ray diffraction, electron probe, and microscopic methods. For the tests at 2600° C the sublimates were collected and chemically analyzed.

Up to 2600° C only HfC vaporized congruently. All compositions containing TaC vaporized incongruently with preferential loss of either carbon or hafnium or both. In these materials the surface compositions changed, because the diffusion of the carbon and hafnium to the surface was not as rapid as their volatilization. These composition changes extended to considerable distances below the surface. At constant temperature the vaporization rate of all compositions containing tantalum decreased with time. This decrease in vaporization rate with heating time became less pronounced at higher temperatures. One explanation for the decrease in vaporization rate with time at constant temperature is that the carbon diffusion rate is less than the vaporization rate up to 2600° C.

INTRODUCTION

The refractory carbides as a class are the highest melting materials known today. As such, they are of interest as potential materials for applications that require high operating temperatures. One possible use of these materials is in the field of emitters for thermionic energy conversion (refs. 1 and 2). However, in this application any incongruently vaporizing material or any material with a relatively high vaporization rate

may be unsuitable. A high vaporization rate may lead to electrical shorting of the cell, and any change in the chemical composition of the surface will alter its electron emission properties (refs. 1 and 2). Therefore, understanding the vaporization rates and processes of carbides is essential if they are to be considered for such uses. The tantalum carbide - hafnium carbide (TaC-HfC) system was selected for vaporization measurements because of the high melting points and low volatilities of its constituents.

In a previous short-time vacuum vaporization-rate study of the TaC-HfC system at 2200° to 2700° C (ref. 3), the preliminary information indicated that the vaporization rate of the 80TaC·20HfC composition (in mole percent) decreased with heating time at constant temperature. Also, a significant change occurred in the lattice parameter of the specimen surface; this change was interpreted as an indication of compositional change.

Other experimental and theoretical results concerning the vaporization of this system have been reported. When TaC is heated at 2600° C or higher in a vacuum, the surface becomes depleted of carbon (ref. 4); that is, it vaporizes incongruently because of the nonequal molar vaporization rates of the constituents of TaC. However, in reference 4, the investigators detected no change in the vaporization rate at constant temperature with heating time. Seigle, Resnick, and Steinitz (ref. 5) concluded that at a constant temperature the vaporization rate of TaC should decrease with heating time because of the decrease in carbon content at the surface of the specimen. At a carbon content of 49 to 49.5 atomic percent, HfC shows no change in its surface composition with heating time over the temperature range of 2200° to 2700° C in a vacuum (ref. 6); that is, it vaporizes congruently. Therefore, the vaporization rate was not time dependent. Kaufman and Stepakoff (ref. 7) have concluded, from calculations based on a model set up for the TaC-HfC system, that all compositions, with the exception of HfC, should vaporize incongruently in a vacuum. They further concluded that, with the exception of HfC, the rates of vaporization of all compositions should decrease with heating time at constant temperature because of changes in surface composition. From their model they calculated for TaC (assuming that only C vaporized) that the rate of vaporization should decrease inversely as the square root of the time. Diffusion was not considered in their model.

The study reported herein was initiated to determine experimentally the type of vaporization in vacuum (congruent or incongruent) as well as the time dependence of the vaporization rate for selected compositions in the TaC-HfC system at several temperatures above 2000° C. The specimens were examined chemically, gravimetrically, microscopically, and by X-ray diffraction and electron-probe methods.

TABLE I. - CHEMICAL ANALYSIS AND X-RAY DIFFRACTION RESULTS OF STARTING MATERIALS IN POWDER FORM[a]

	TaC		HfC		80TaC · 20HfC	
	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Analysis, weight percent:						
Total C	5.98		6.20		5.85	
Free C	0.11		0.01		0.03	
Combined C	5.87	6.22	6.19	6.30	5.82	6.23
Ta	----	93.78	----		74.23	75.21
Hf	----		93.72	93.70	18.92	18.56
W	0.11		----		-----	
Fe	----		<0.005		0.036	
Si	<0.01		<0.01		<0.001	
Nb	0.52		----		0.32	
Ti	----		----		0.13	
Zr	<0.01		<0.01		0.16	
Co	0.057		----		----	
Cr	0.051		----		----	
B	Not detected		<0.005		<0.003	
O_2	0.19		0.007		0.18	
N_2	0.005		0.014		0.021	
H_2	----		0.0031		0.012	
Formula	$(Ta_{0.988}Nb_{0.011}W_{0.001})C_{0.932}$	$TaC_{1.0}$	$HfC_{0.982}$	$HfC_{1.0}$	$(Ta_{0.782}Hf_{0.202}Nb_{0.007}Ti_{0.005}Zr_{0.004})C_{0.925}$	$(Ta_{0.8}Hf_{0.2})C_{1.0}$
C, at. %	48.2	50	49.6	50	47.9	50
C/Metal	0.932	1.0	0.982	1.0	0.925	1.0
Lattice parameter[b], Å	4.455 (±0.001)	----	4.640 (±0.001)	----	4.483 (±0.001)	----
Fisher particle size, μ	3.3	----	2.75	----	4.2	----

[a]All three compositions are single-phase face-centered-cubic materials.

[b]Lattice parameter accuracy is standard deviation.

EXPERIMENTAL PROCEDURE

Materials and Specimen Preparation

Table I presents the results of chemical and X-ray diffraction investigations on the commercially supplied powder starting materials. These three materials are referred to nominally as TaC, HfC, and 80TaC·20HfC.

In addition to these three materials, compositions of 50 mole percent $TaC_{0.96}$ and 50 mole percent $HfC_{0.96}$ and of 25 mole percent $TaC_{0.97}$ and 75 mole percent $HfC_{0.97}$ were prepared by mixing TaC and HfC in the proper ratios before the specimens were formed. These compositions are referred to nominally as 50TaC·50HfC and 25TaC·75HfC.

Solid cylindrical pieces (90 to 98 percent theoretical density) were formed by hot-pressing the carbide powders in graphite dies at 2600° C for 1 hour in an argon atmosphere. From these cylinders, specimens of 15.6-millimeter outside diameter by 9.3-millimeter inside diameter by 6.2-millimeter long were fabricated by electric discharge machining. An approximate blackbody hole with a depth-to-diameter ratio of about 5 was drilled in the ring parallel to its length. Free carbon was removed from the surface of the specimens by grinding on 600 silicon carbide abrasive cloth. Oil used in discharge machining was removed with organic solvents. (Further details on sample preparation are given in ref. 3.)

X-ray diffraction examination of all hot-pressed compositions showed them to be single phase, face-centered cubic, solid solutions. Also, metallographic examination revealed no second phase. The lattice parameters of the hot-pressed carbides are given in table II. The larger standard deviations for the 50TaC·50HfC and 25TaC·75HfC compositions are due to the broader diffraction peaks and lack of resolution of the α_1, α_2 lines. The chemical compositions of the hot-pressed specimens were assumed to be the same as those of the starting powders, since TaC, HfC, and the 80TaC·20HfC specimens showed no significant changes in their lattice parameters after hot-pressing.

TABLE II. - LATTICE PARAMETERS OF HOT-PRESSED CARBIDES

Composition	Lattice parameter, a_o, Å (a)
TaC	4.456 (±0.001)
80TaC·20HfC	4.482 (±0.001)
50TaC·50HfC	4.552 (±0.005)
25TaC·75HfC	4.590 (±0.008)
HfC	4.640 (±0.001)

[a]Lattice parameter accuracy is standard deviation.

All X-ray diffraction patterns were obtained with a diffractometer at a scanning speed of 1/2° per minute (2θ) with nickel-filtered copper radiation. A computer was used to obtain the lattice parameters by means of the least squares extrapolation of Cohen as modified by Hess (ref. 8). All diffraction peaks were included in these calculations.

Vaporization Measurements

The vaporization-rate measurements were conducted in a continuously evacuated, vertical, water-cooled, fused quartz-tube induction furnace, which is described in reference 9. The specimen was supported on three 60-mil-diameter tungsten rods and was heated directly.

The temperature of the specimen was measured with a disappearing-filament optical pyrometer, which had been calibrated against a standard tungsten filament lamp (NBS standard) with all optical elements in the light path.

A typical vaporization-rate determination involved weighing the specimen to the nearest 0.2 milligram, inserting the specimen into the furnace tube, and evacuating to 10^{-6} torr (cold cathode gage). The specimen was heated in 5 minutes to the desired test temperature. This temperature was maintained to within $\pm 20^{\circ}$ C for the desired length of time at a pressure of less than 8×10^{-6} torr. At the end of the heating period the power to the furnace was turned off, and the specimen cooled to less than 600° C in 5 minutes. The specimen, after cooling to room temperature, was removed and reweighed. This process was repeated as long as desired or until the specimen cracked. The weight loss per unit of geometrical surface area (g/cm^2) was calculated for each heating period by using the effective specimen area calculated by the procedure given in reference 3. The cumulative weight loss (g/cm^2) was plotted against the cumulative heating time (sec) on linear coordinates. Since this relation is nonlinear, tangents to this curve were constructed at various heating times; therefore, the slope of the tangent is the instantaneous vaporization rate ($g/(cm^2)(sec)$).

Postheating Examinations

To understand the vaporization processes involved, the surface and interior compositions of the specimen were obtained from X-ray diffraction and electron microprobe data as functions of total heating time. Hence, between each weight-loss determination an X-ray diffraction pattern of the surface was obtained (see fig. 1 for orientation). The phases present were identified and the lattice parameters were determined as accurately as possible. Because of penetration by the X-ray beam (estimated to be about 10μ), these results are not necessarily those of the true surface of the specimen.

For study of compositional changes, those specimens which had previously been heated at 2600° C were mounted in plastic. Initially, 0.025-millimeter-thick layers were removed from the top of the cylindrical specimen with a diamond abrasive wheel (fig. 1). An X-ray diffraction pattern of this newly exposed surface was made. Repeating this process determined the change in composition from the top to the center of the specimen. As the vertical distance increased, larger increments were removed.

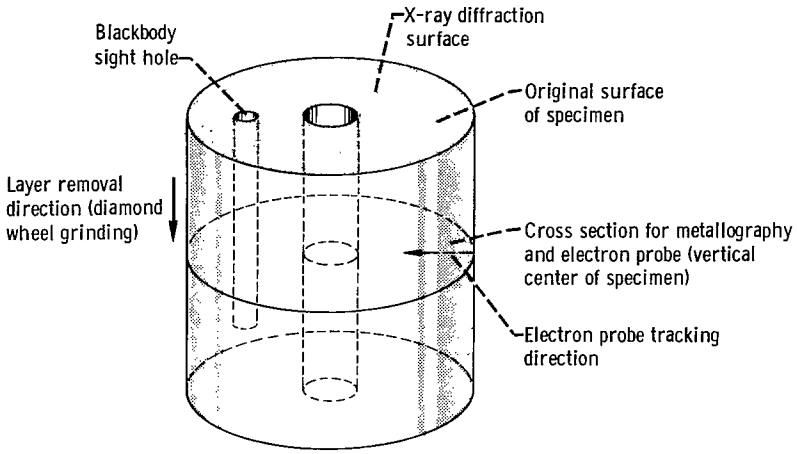


Figure 1. - Schematic diagram of test specimen for orientation of postheating examinations (not to scale).

The cross section (at the vertical center of the specimen) was examined by the electron-beam microprobe method for both Hf and Ta content by tracking from the outer cylindrical edge toward the center (fig. 1). The surface of the cross section was given a metallographic polish, was coated with an aluminum film (to give uniform surface conductivity), and was simultaneously scanned for Hf and Ta content on a dual-channel instrument scanning at 8 microns per minute with an 8-micron-diameter beam. The results over the first 8 to 10 microns from the specimen edge were not usable because of rounding of the edge during polishing.

For metallographic examination, the electron-probe specimens were repolished and etched with an aqueous solution of hydrofluoric and sulfuric acids. All specimens were examined at a magnification of 250.

For each of the 2600° C runs, the sublimate was brushed from the furnace tube, collected, and analyzed. Chemical determination of total carbon was done on each sample; hafnium was determined when possible, and tantalum, when present, was determined by difference. This determination by difference was necessary because of the small amount of sample (approx 150 mg). The analytical data for any sublimate specimen have a total error of less than 10 percent and are probably accurate to within ±3 percent. The major impurities in the sublimates were silicon, iron, and chromium. The total impurities were less than 1 percent. A material balance was not obtained; that is, the weight of the collected sublimate was always 10 to 20 percent less than the weight lost by the specimen. This difference can be caused by (1) incomplete removal of the sublimate from the tube wall, (2) chemical reaction of the sublimate with the furnace tube, (3) a noncondensable vapor species, or (4) a combination of these possibilities. A chemical reaction of the sublimate with the furnace tube or the presence of a noncondensable vapor species would lead to incorrect sublimate compositions. Since no condensate was found in the liquid-

nitrogen cold trap of the vacuum system and no permanent discoloration of the quartz furnace tube was observed, it is believed that these two possible causes are not the major factors for the lack of a material balance. Although a material balance was not obtained, the vaporization rates by weight loss are correct and the chemical composition of the sublimates support the composition changes in the solid.

RESULTS

Vaporization Rates

The vaporization rate - heating time data points of all compositions for each temperature studied were plotted on log-log coordinates. To these points a straight line was fitted with a least-squares computer program. The results of these operations are presented in figure 2 for the 80TaC· 20HfC composition. The vaporization rates were fitted to the rate equation $R = A/t^n$, where R is the vaporization rate ($g/(cm^2)(sec)$), t is time (hr), and A and n are constants for a given temperature. The least squares values of A and n, along with their time range of validity, are given in table III for each composition and temperature studied.

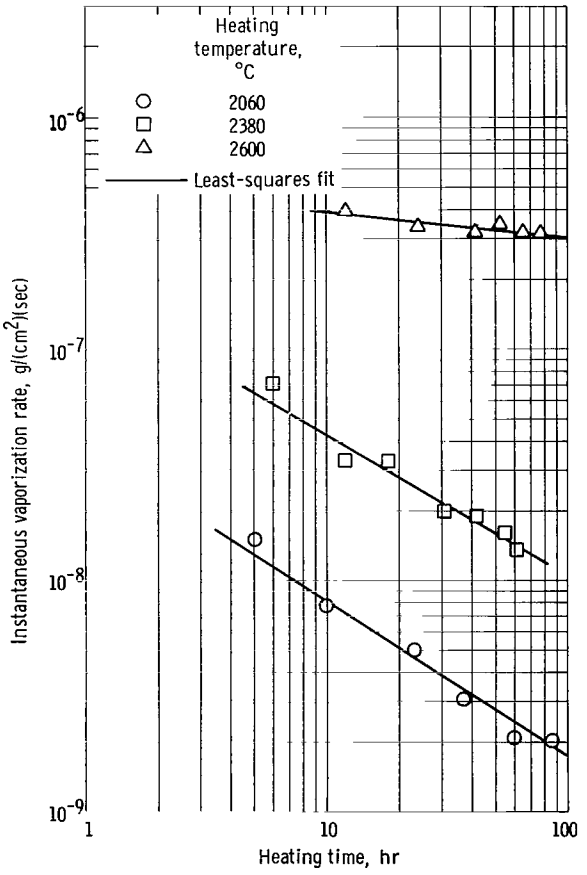


Figure 2. - Effect of heating time on vaporization rate for 80-percent tantalum carbide - 20-percent hafnium carbide composition in vacuum.

The data of figure 2 indicate that the vaporization rate of the 80TaC· 20HfC composition decreases with heating time at 2060°, 2380°, and 2600° C. The rate of decrease is greater at 2060° and 2380° than at 2600° C. Table III presents, in analytical form, the same general trends for TaC, 50TaC· 50HfC, and 25TaC· 75HfC as were observed for the 80TaC· 20HfC composition. However, no change in the vaporization rate of HfC occurs with heating time, as evidenced by zero values of n at all temperatures.

Postheating Examinations

Sublimates collected at 2600° C. - The chemical analyses for the sublimates collected

TABLE III. - CONSTANTS OF VAPORIZATION RATE EQUATION[a]

Carbide	Temperature, °C	A (b)	n (b)	Valid time range, hr
TaC	2060	5.33×10^{-8}	0.61	5 to 60
	2230	5.70×10^{-8}	.36	8 to 75
	2380	1.24×10^{-7}	.37	6 to 30
	2600	8.5×10^{-7}	.10	10 to 24
80TaC · 20HfC	2060	3.86×10^{-8}	0.69	5 to 85
	2380	1.70×10^{-7}	.59	6 to 60
	2600	5.0×10^{-7}	.11	12 to 77
50TaC · 50HfC	2060	7.15×10^{-8}	1.02	5 to 82
	2230	1.8×10^{-7}	1.07	6 to 45
	2380	1.2×10^{-7}	.39	3 to 35
	2600	6.5×10^{-7}	.16	8 to 30
25TaC · 75HfC	2380	1.4×10^{-7}	0.32	3 to 30
	2600	1.2×10^{-6}	.10	12 to 32
HfC	2060	1.5×10^{-8}	0	10 to 72
	2450	1.5×10^{-6}	0	3 to 25
	2600	4.6×10^{-6}	0	10 to 30

[a] $R = A/t^n$ where R is vaporization rate $(g/(cm^2)(sec))$; A and n are constants; t is time (hr).

[b] Least-squares fit.

from each composition after successively longer heating periods at 2600° C are compiled in table IV. Although the reliability of the values presented is not considered to be better than ±10 percent, the values can be used to indicate certain trends. It is evident that the sublimates of all Ta-containing compositions have more carbon than the original carbides and that the descending order of volatility of the constituents is C, Hf, and Ta. Within the limits of reliability of the data, the sublimates from HfC contain the same proportions of C and Hf as the original carbide.

From the sublimate compositions given in table IV and the appropriate vaporization rates, the molar vaporization rates of C, Ta, Hf, and total metal (Ta + Hf) were calculated for a heating time of 20 hours. These results are presented graphically in figure 3 in order to facilitate direct comparison of the data. For the sake of clarity, the results

TABLE IV. - CHEMICAL COMPOSITION OF SUBLIMATES COLLECTED FROM TANTALUM CARBIDE - HAFNIUM CARBIDE SOLUTIONS AFTER VARIOUS HEATING TIMES AT 2600° C IN VACUUM

Carbide	Element	Original composition, at. % (a)	Cumulative heating time, hr	Sublimate, at. % (a)	Sublimate / Original, at. % / at. %
TaC	Ta	51.4	10	[b]6	0.117
			16	[b]10	.195
			24	[b]12.5	.243
	Total C	48.6	10	94	1.93
			16	90	1.85
			24	87.5	1.80
80TaC · 20HfC	Ta	40.9	20	[b]4.8	0.117
	Hf	10.6	20	10.8	1.02
	Total C	48.5	20	84.4	1.74
			53	72	1.48
			65	70	1.44
			77	66	1.36
	Hf + Ta	51.5	20	15.6	0.303
			53	[b]28	.54
			65	[b]30	.58
			77	[b]34	.66

[a]Impurity elements omitted.
[b]By difference. (Impurity elements, which were less than 1%, were ignored.)

TABLE IV. - Concluded. CHEMICAL COMPOSITION OF SUBLIMATES COLLECTED FROM TANTALUM CARBIDE - HAFNIUM CARBIDE SOLUTIONS AFTER VARIOUS HEATING TIMES AT 2600° C IN VACUUM

Carbide	Element	Original composition, at. % (a)	Cumulative heating time, hr	Sublimate, at. % (a)	Sublimate / Original, at. % / at. %
50TaC · 50HfC	Ta	25.5	17.5	[b]8.0	0.31
			28	[b]8.2	.32
	Hf	25.5	17.5	21.7	0.85
			28	19.8	.78
	Total C	49.0	8	74	1.51
			17.5	70.3	1.43
			28	72	1.47
	Hf + Ta	51.0	8	[b]26	0.51
			17.5	[b]29.7	.58
			28	[b]28	.55
25TaC · 75HfC	Ta	12.7	12	[b]3.6	0.28
			23	[b]1.8	.14
	Hf	38.1	12	34.4	0.90
			23	42.2	1.11
	Total C	49.2	12	62.0	1.26
			23	56.0	1.14
			32	60	1.22
	Hf + Ta	50.8	12	[b]38	0.75
			23	[b]44	.87
			32	[b]40	.79
HfC	Hf	50.4	12	[b]48.7	0.97
			30	[b]50	.99
	Total C	49.6	12	51.3	1.03
			30	50	1.01

[a]Impurity elements omitted.

[b]By difference. (Impurity elements, which were less than 1%, were ignored.)

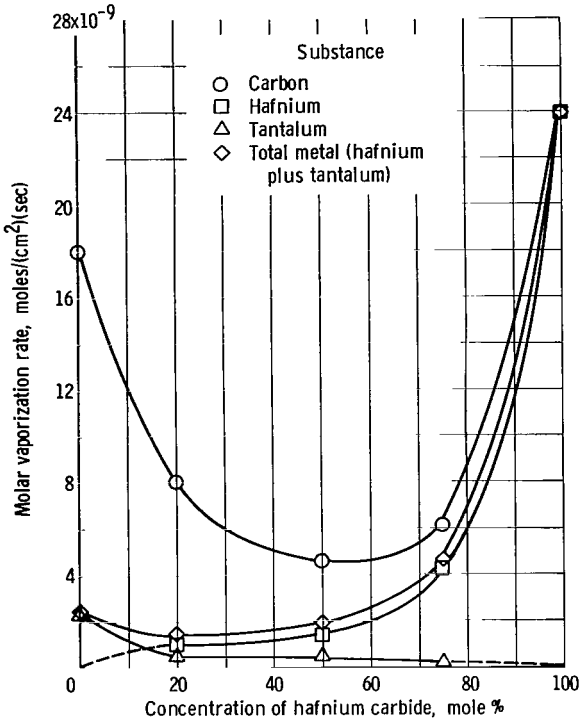


Figure 3. - Molar vaporization rates of carbon, hafnium, tantalum, and total metal (hafnium plus tantalum) for tantalum carbide - hafnium carbide at 2600° C in vacuum. Calculated from 20-hour sublimate compositions and instantaneous vaporization rate.

will be stated again: All compositions containing Ta vaporize incongruently, while HfC is the only composition that vaporizes congruently.

X-ray diffraction of specimen surfaces. - The specimen surface after heating was examined by X-ray diffraction. In this way newly formed phases, if present in sufficient concentration, can be detected, and changes in the lattice parameter can be measured. Figure 4 indicates that the lattice parameter of the face-centered cubic phase in the specimen surface of both TaC and the 80TaC· 20HfC composition decreases with heating time at 2380° and 2600° C. Also, after a sufficiently long heating time at 2600° C, the lattice parameter of the face-centered cubic phase for both the TaC and 80TaC· 20HfC compositions reached a minimum value between 4. 41 and 4. 42 angstroms, and a second phase of hexagonal crystal structure was detected. The lattice parameters of this hexagonal phase were very nearly those of Ta_2C for both compositions. For TaC the lattice parameter values of the face-centered cubic phase could be converted into carbon content in the specimen surface by using the data of Bowman (ref. 10). These results are plotted in figure 4. Obviously, the carbon content of the surface decreases with heating time. For the 80TaC· 20HfC composition converting the surface lattice parameter values of the face-

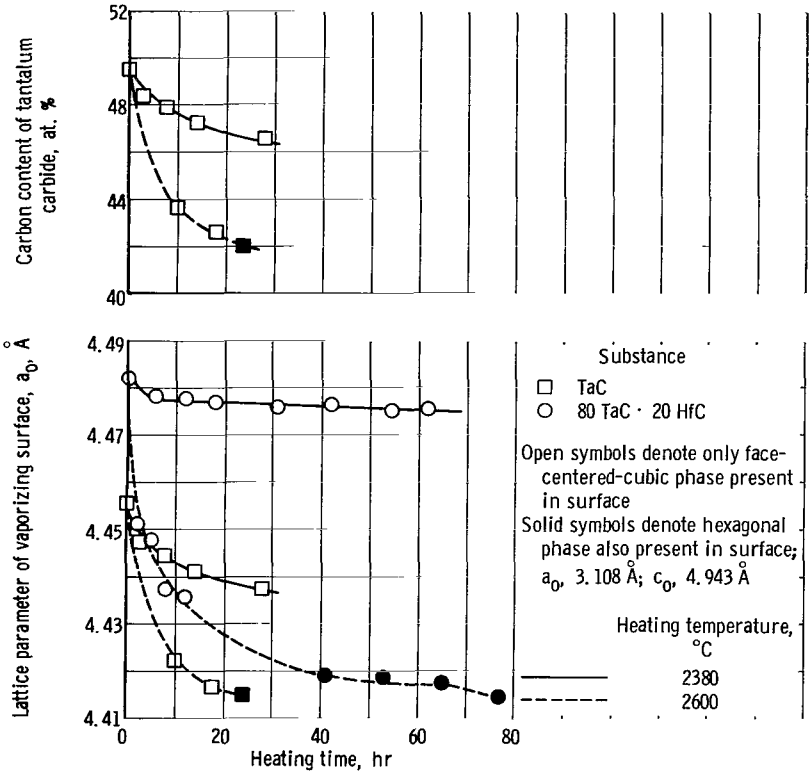


Figure 4. - Variation of lattice parameter and carbon content of vaporizing surface of tantalum carbide and 80-percent tantalum carbide - 20-percent hafnium carbide after various heating times in vacuum.

centered cubic phase to composition was not possible, but reference 11 shows that a decrease in either C or Hf content or both (of compositions in the face-centered cubic area of the Ta-Hf-C phase diagram), causes a decrease in the lattice parameter. We can therefore conclude that the decrease in the lattice parameter of the surface of the 80TaC· 20HfC composition with heating time is due to a composition change. Similar decreases with heating time were found in the surface lattice parameters for the 50TaC· 50HfC and 25TaC· 75HfC compositions. With heating time, however, HfC showed no change in its surface lattice parameter greater than the standard deviation (±0. 001 Å).

Internal Examinations

Having established the fact that the chemical composition of the surface changes, an examination of several specimens by X-ray diffraction and electron-probe techniques was made to determine the vertical extent of these changes (see fig. 1, p. 6, for orientation). The TaC specimen was examined after 24 hours at 2600° C; the results are given in figure 5. The carbon content was calculated from the lattice parameters of the face-

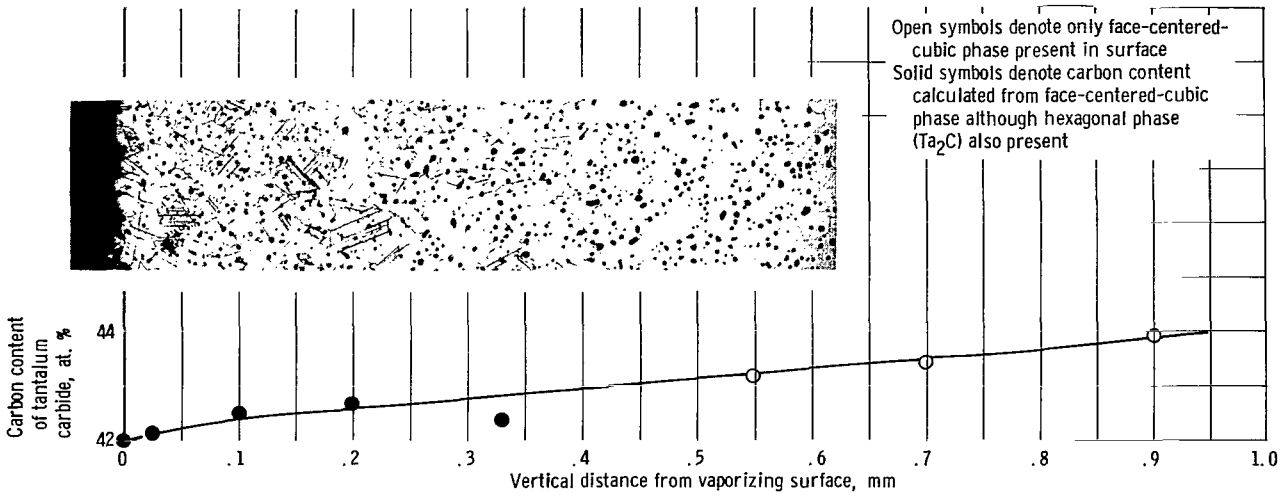


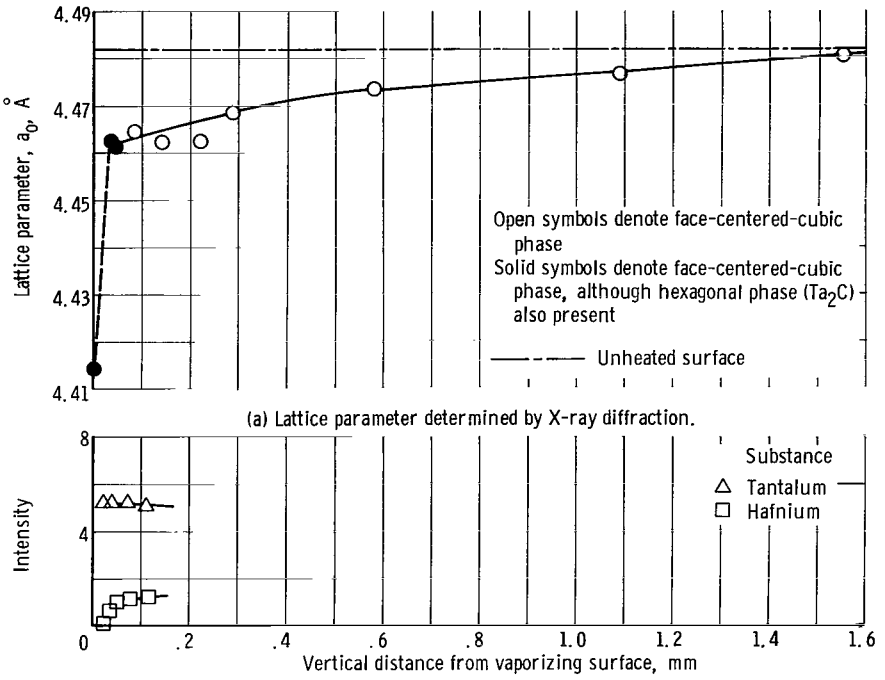
Figure 5. - Variation of appearance of cross section and carbon content (determined from lattice parameters) for tantalum carbide heated 24 hours at 2600° C in vacuum. Sample etched; X250; reduced 40 percent in printing.

centered cubic phase at various depths using the data of Bowman (ref. 10). It is evident that a carbon gradient exists. A photomicrograph of the surface region shows that a striated, second phase is present and that it disappears at approximately the same distance below the surface at which the hexagonal (Ta_2C) phase disappears from the X-ray patterns.

An electron-probe and X-ray diffraction study at various depths was made on the 80TaC·20HfC composition after it was heated for 77 hours at 2600° C; the results are presented in figure 6. There was a very steep increase in the lattice parameter and Hf content in the first 0.02 to 0.03 millimeter below the surface. The lattice parameter then increased more slowly until it reached the initial value at or near the vertical center of the specimen. A microscopic inspection of the cross section revealed a high density of striations near the surface similar to those observed in TaC. These striations disappeared at approximately the same depth at which the hexagonal (Ta_2C) phase was no longer detected in the X-ray patterns. Experimental results similar to these were obtained for the 50TaC·50HfC and 25TaC·75HfC compositions after they were heated at 2600° C for 30 hours. For HfC no significant changes with depth were observed in the lattice parameter or Hf concentration gradient after 30 hours at 2600° C.

DISCUSSION

From the experimental results, it is possible to construct the general vaporization process for this system. The elements of all the compositions, except HfC, vaporize incongruently and cause the chemical composition of the surface to change when the diffusion rate is not sufficient to replace the elements lost by vaporization. The presence



(a) Lattice parameter determined by X-ray diffraction.

(b) Concentration gradients determined by electron probe.

Figure 6. - Variation of lattice parameter of face-centered-cubic phase and metal (tantalum and hafnium) content with vertical distance from vaporizing surface for composition of 80-percent tantalum carbide - 20-percent hafnium carbide after heating for 77 hours at 2600° C in vacuum.

of the concentration gradients implies that the rate of supply to the surface of the volatilized elements by diffusion is less than their vaporization rates. This difference in rates, then, shifts the surface composition in the direction of lower C and Hf contents over the temperature range studied.

The decrease in the vaporization rate with heating time at a constant temperature is explained as follows: At zero time the composition of the surface and the bulk are equal, but after heating for some time t_1 a concentration gradient is set up. Thus, the next vaporization-rate value is less than the first, since less C and Hf are present to be vaporized because they were not replaced by diffusion. Therefore, each time the specimen is heated, the value of the rate is less, because vaporization is now taking place from a new surface composition, which contains less C and Hf than the previous one.

The decrease in vaporization rate with heating time is temperature dependent, with the decrease less pronounced at higher temperatures. It is proposed that at some temperature, higher than that studied here, the diffusion rate of C will become equal to its vaporization rate, and then the vaporization rate will remain constant for some time. However, because C is vaporizing incongruently at this higher temperature, the depletion must be taking place in the interior of the specimen.

SUMMARY OF RESULTS

A study of the vacuum vaporization rates for selected compositions in the tantalum carbide - hafnium carbide (TaC-HfC) system at temperatures above 2000° C gave the following results:

1. The vaporization rate of TaC, 80TaC·20HfC, 50TaC·50HfC, and 25TaC·75HfC at 2060° to 2600° C decreased with increased heating time. This decrease in vaporization rate is due to the incongruent vaporization of these compositions. The descending order of volatility of the elements from these compositions is C, Hf, and Ta. The composition of the surface of these carbides changed with heating time because the diffusion rate of the volatilized elements is slower than their vaporization rate as demonstrated by the concentration gradients. Therefore, the vaporization process for this system is diffusion controlled.

2. The vaporization rate of HfC in this same temperature range is independent of heating time. This independence is due to the congruent vaporization of HfC.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 28, 1966.

REFERENCES

1. Yang, Ling; and Carpenter, F. D.: Materials Problems in Cesium Thermionic Converters. J. Electrochem. Soc., vol. 108, no. 11, Nov. 1961, pp. 1079-1086.

2. Stephas, Paul: Search for a Nuclear Thermionic Emitter. Nucleonics, vol. 19, no. 12, Dec. 1961, pp. 66; 70-73.

3. Deadmore, Daniel L.: Vaporization of Tantalum-Carbide - Hafnium-Carbide Solid Solutions at 2500° to 3000° K. NASA TN D-2512, 1964.

4. Coffman, J. A.; Kibler, G. M; Riethof, T. R.; and Watts, A. A.: Carbonization of Plastics and Refractory Materials Research. Rept. No. TR 60-646, pt. I, WADD, Feb. 1961, pp. 40-53.

5. Seigle, L.; Resnick, R; and Steinitz, R.: Dissociation and Evaporation of TaC, HfC and ZrC at Elevated Temperatures. Tech. Memo. No. 62-475.2, General Telephone and Electronics Labs., Inc., Nov. 9, 1962.

6. Coffman, J. A.; Coulson, K. L.; and Kibler, G. M.: Carbonization of Plastics and Refractory Materials Research. Rept. No. QPR-5, General Electric Co., Mar. 31, 1961, pp. 14-19.

7. Kaufman, L.; and Stepakoff, G.: Computational Methods for Calculation of Rates of Evaporation in the Ta-Hf-C System. Manlabs, Inc., (NASA CR-54910), 1964.

8. Hess, James B.: A Modification of the Cohen Procedure for Computing Precision Lattice Constants from Powder Data. Acta Cryst., vol. 4, 1951, pp. 209-215.

9. May, Charles E.; Koneval, Donald; and Fryburg, George C.: Stability of Ceramics in Hydrogen Between 4000° and 4500° F. NASA MEMO 3-5-59E, 1959, p. 12.

10. Bowman, Allen L.: The Variation of Lattice Parameter with Carbon Content of Tantalum Carbide. J. Phys. Chem., vol. 65, no. 9, Sept. 27, 1961, pp. 1596-1598.

11. Deadmore, D. L.; and Zaplatynsky, I.: The Ternary System Tantalum-Hafnium-Carbon at 2050° C. NASA TN D-2768, 1965.

NASA-Langley, 1966 E-3203

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

TECHNICAL REPRINTS: Information derived from NASA activities and initially published in the form of journal articles.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546